Hydrogen physisorption and intercalation in novel nano-porous graphites

Massimiliano Bartolomei[†] , Estela Carmona-Novillo[†] , Giacomo Giorgi[§]

[†] Institute of Fundamental Physics, IFF_CSIC, Serrano 123, 28006 Madrid, Spain
[§] Department of Chemical System Engineering,School of Engineering, University of Tokyo, Japan

maxbart@iff.csic.es

Pristine graphene is in principle an ideal adsorbing material due to its large specific area, stability, mechanical properties and low weight. Nevertheless, it has been theoretically demonstrated that molecular hydrogen (H_2) physisorption on graphene is not particularly favourable, being tha adsorption energy, mainly determined by van der Waals interactions, around 0.05 eV. Intercalation between graphene layers could lead to more encouraging adsorption energies but, unfortunately, in pure graphite there is no room for any atomic or molecular species to be hosted.
A possible solution to this problem is the use of porous derivative of graphene as “building blocks” to construct a new class of porous graphites characterized by a larger interlayer volume available for gas storage. To this regard graphynes, which are novel two-dimensional (2D) carbon-based materials, represent promising candidates since they naturally exhibit a nanoweb-like structure characterized by triangular and regularly distributed subnanometer pores[1]. These intriguing features make them appealing for molecular filtering as shown by recent theoretical predictions[2].
The possibility to exploit graphynes as ideal media for the H_2 reversible storage is here theoretically studied. First principles adsorption energies of H_2 on graphene, graphdiyne and graphtriyne molecular prototypes are obtained at the MP2C[3] level of theory. First, the case of a single layer is investigated and it is found that graphynes are more suited than graphene for H_2 physical adsorption since they provide larger binding energies at equilibrium distances much closer to the 2D plane. In particular, for graphtriyne a flat minimum located right in the geometric center of the pore is identified.
A novel graphite composed of graphtriyne stacked sheets is then proposed[4] and an estimation of its 3D arrangement is obtained at the DFT level of theory by considering a periodic model of the involved bilayers. In contrast to pristine graphite this new carbon material allow both H_2 intercalation and out-of-plane diffusion by exploiting the larger volume provided by its nanopores. Related H_2 binding energies for intercalation and in-pore adsorption are around 0.1 eV (see Figure) and they could lead to high storage capacities exceeding those found to date for carbon nanostructures of different nature. The proposed layered carbon allotrope should be considered as a promising material for a safer and potentially cheaper alternative for hydrogen on-board storage than conventional solutions based on cryogenic liquefaction and/or high compression.

References

[1] G. Li *et al*., *Chem. Commun.*, **46**, 3256-3258 (2010)
[2] M. Bartolomei *et al.*, *J. Phys. Chem*. *Lett.*, **5**, 751-755 (2014); *J. Phys. Chem*. *C*, **118**, 29966-29972 (2014)
[3] M. Pitonák and A. Hesselmann, *J. Chem. Theory Comput. Chem*., **6**, 168-178 (2010)
[4] M. Bartolomei *et al.*, *Carbon*, **95**, 1076-1081 (2015)

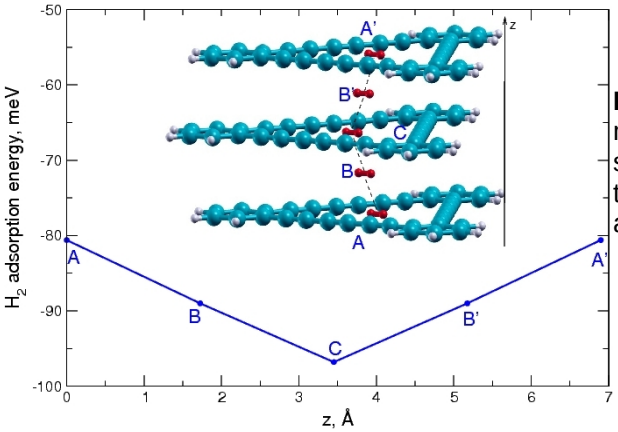

Figure Adsorption energy evolution of one H_2 molecule crossing a porous graphite composed of stacked graphtriyne layers. A prototype consisting of three parallel graphtriyne pores in a Bernal-like 3D arrangement is used.